

CLAIMS

What is claimed is:

1. A composition comprising a plurality of carbon fibers bearing nanoparticles.
- 5 2. The composition of claim 1, wherein said nanoparticles are selected from the group consisting of nanotubes, nanofibers, nanohorns, nanopowders, nanospheres, and quantum dots.
3. The composition of claim 1, wherein said nanoparticles are carbon nanotubes.
- 10 4. The composition of claim 1, wherein said plurality of carbon fibers comprise a porous electrode.
5. The composition of claim 1, wherein said plurality of carbon fibers comprise a carbon paper.
6. The composition of claim 3, wherein said carbon nanotubes are
15 seeded with one or more catalysts selected from the group consisting of $\text{Co}_{1-x}\text{Mo}_x$ where $0 \leq x \leq 0.3$, $\text{Co}_{1-x-y}\text{Ni}_x\text{Mo}_y$ where $0.1 \leq x \leq 0.7$ and $0 \leq y \leq 0.3$, $\text{Co}_{1-x-y-z}\text{Ni}_x\text{V}_y\text{Cr}_z$ where $0 \leq x \leq 0.7$ and $0 \leq y \leq 0.2$, $0 \leq z \leq 0.2$, $\text{Ni}_{1-x-y}\text{Mo}_x\text{Al}_y$ where $0 \leq x \leq 0.2$ and $0 \leq y \leq 0.2$, and $\text{Co}_{1-x-y}\text{Ni}_x\text{Al}_y$ where $0 \leq x \leq 0.7$ and $0 \leq y \leq 0.2$.
7. The composition of claim 3, wherein said carbon nanotubes are
20 seeded with one or more catalysts selected from the group consisting of $\text{Co}_{8.8}\text{Mo}_{1.2}$, $\text{Co}_{2.2}\text{Ni}_{5.6}\text{Mo}_{2.2}$, $\text{Co}_{5.7}\text{Ni}_{2.1}\text{V}_{1.1}\text{Cr}_{1.1}$, $\text{Ni}_{8.0}\text{Mo}_{1.0}\text{Al}_{1.0}$, and $\text{Co}_{6.4}\text{Ni}_{2.4}\text{Al}_{1.2}$.
8. The composition of claim 3, wherein said nanoparticles are nanotubes having a length less than $50 \mu\text{m}$ and a width less than about 100 nm .
9. The composition of claim 3, wherein said nanoparticles are
25 nanotubes having a diameter of about 50 nm to about 100 nm .

10. The composition of claims 1 or 3, wherein said nanoparticles are coated with a substantially continuous thin film comprising platinum or a platinum alloy.

11. The composition of claim 10, wherein said thin film partially covers the nanoparticles.

5 12. The composition of claim 10, wherein the nanoparticles are fully coated with said thin film.

13. The composition of claim 10, wherein said thin film ranges in thickness from about 1 to about 1000 angstroms.

10 14. The composition of claim 13, wherein said thin film ranges in thickness from about 5 to about 500 angstroms.

15. The composition of claim 13, wherein said thin film ranges in thickness from about 5 to about 100 angstroms.

15 16. The composition of claim 15, wherein said thin film comprises an alloy comprising platinum (Pt), vanadium (V), and one or more metals selected from the group consisting of Co, Ni, Mo, Ta, W, and Zr.

17. The composition of claim 16, wherein said thin film comprises an alloy comprising platinum (Pt), vanadium (V), and one or more metals selected from the group consisting of Co, and Ni.

20 18. The composition of claim 16, wherein platinum comprises up to about 50% (mole ratio or atomic percentage) of said alloy.

19. The composition of claim 16, wherein platinum comprises up to about 12% (mole ratio or atomic percentage) of said alloy.

20. The composition of claim 16, wherein said alloy contains platinum, vanadium, nickel, and copper.

25 21. The composition of claim 16, wherein said thin film comprises an alloy having the formula:



wherein:

x is greater than 0.06 and less than 1;

y, z, and w are independently greater than zero and less than 1;

x + y + z + w = 1.

22. The composition of claim 21, wherein x is 0.12.

23. The composition of claim 21, wherein x is 0.12, y is 0.07, z is 0.56, and w is 0.25.

24. A fuel cell catalyst comprising a plurality of nanoparticles said nanoparticles coated with a substantially continuous thin film comprising platinum or a platinum alloy.

25. The fuel cell catalyst of claim 24, wherein said thin film partially covers the nanoparticles.

26. The fuel cell catalyst of claim 24, wherein the nanoparticles are fully coated with said thin film.

27. The fuel cell catalyst of claim 24, wherein said thin film ranges in thickness from about 1 to about 1000 angstroms.

28. The fuel cell catalyst of claim 27, wherein said thin film ranges in thickness from about 5 to about 500 angstroms.

29. The fuel cell catalyst of claim 27, wherein said thin film ranges in thickness from about 5 to about 100 angstroms.

30. The fuel cell catalyst of claim 24, wherein said thin film comprises an alloy comprising platinum (Pt), vanadium (V), and one or more metals selected from the group consisting of Co, Ni, Mo, Ta, W, and Zr.

31. The fuel cell catalyst of claim 30, wherein said thin film comprises an alloy comprising platinum (Pt), vanadium (V), and one or more metals selected from the group consisting of Co, and Ni.

32. The fuel cell catalyst of claim 30, wherein platinum comprises up to
5 about 50% (mole ratio or atomic percentage) of said alloy.

33. The fuel cell catalyst of claim 30, wherein platinum comprises up to about 12% (mole ratio or atomic percentage) of said alloy.

34. The fuel cell catalyst of claim 33, wherein said alloy contains platinum, vanadium, nickel, and copper.

10 35. The fuel cell catalyst of claim 30, wherein said thin film comprises an alloy having the formula:



wherein:

15 x is greater than 0.06 and less than 1;
y, z, and w are independently greater than zero and less than 1;
x + y + z + w = 1.

36. The fuel cell catalyst of claim 35, wherein x is 0.12.

37. The fuel cell catalyst of claim 35, wherein x is 0.12, y is 0.07, z is 0.56, and w is 0.25.

20 38. The fuel cell catalyst of claim 24, wherein said nanoparticles are attached, or incorporated into, a substrate.

39. The fuel cell catalyst of claim 38, wherein said nanoparticles are attached, or incorporated into, a porous carbon substrate.

25 40. The fuel cell catalyst of claim 38, wherein said nanoparticles are attached, or incorporated into, to a porous electrically conducting substrate.

41. The fuel cell catalyst of claim 38, wherein said nanoparticles are electrically coupled to an electrode.

42. The fuel cell catalyst of claim 38, wherein said nanoparticles are attached to a polymer substrate.

5 43. The fuel cell catalyst of claim 38, wherein said nanoparticles are carbon nanotubes and said nanotubes are attached to or contacting carbon fibers.

44. The fuel cell catalyst of claim 24, wherein said nanoparticles are selected from the group consisting of nanotubes, nanofibers, nanohorns, nanopowders, nanospheres, and quantum dots.

10 45. The fuel cell catalyst of claim 24, wherein said nanoparticles are carbon nanotubes.

46. The composition of claim 24, wherein said carbon nanotubes are seeded with one or more catalysts selected from the group consisting of $\text{Co}_{1-x}\text{Mo}_x$ where $0 \leq x \leq 0.3$, $\text{Co}_{1-x-y}\text{Ni}_x\text{Mo}_y$ where $0.1 \leq x \leq 0.7$ and $0 \leq y \leq 0.3$, $\text{Co}_{1-x-y-z}\text{Ni}_x\text{V}_y\text{Cr}_z$ where $0 \leq x \leq 0.7$ and $0 \leq y \leq 0.2$, $0 \leq z \leq 0.2$, $\text{Ni}_{1-x-y}\text{Mo}_x\text{Al}_y$ where $0 \leq x \leq 0.2$ and $0 \leq y \leq 0.2$, and $\text{Co}_{1-x-y}\text{Ni}_x\text{Al}_y$ where $0 \leq x \leq 0.7$ and $0 \leq y \leq 0.2$.

47. The composition of claim 24, wherein said carbon nanotubes are seeded with one or more catalysts selected from the group consisting of $\text{Co}_{8.8}\text{Mo}_{1.2}$, $\text{Co}_{2.2}\text{Ni}_{5.6}\text{Mo}_{2.2}$, $\text{Co}_{5.7}\text{Ni}_{2.1}\text{V}_{1.1}\text{Cr}_{1.1}$, $\text{Ni}_{8.0}\text{Mo}_{1.0}\text{Al}_{1.0}$, and $\text{Co}_{6.4}\text{Ni}_{2.4}\text{Al}_{1.2}$.

20 48. The fuel cell catalyst of claim 45, wherein said nanoparticles are nanotubes having a length less than about 200 μm and a width less than about 100 nm.

49. The fuel cell catalyst of claim 45, wherein said nanoparticles are nanotubes having a diameter of about 10 nm to about 100 nm.

25 50. An electrode-membrane combination comprising:
at least a first conductive electrode comprising a first fuel cell catalyst;

at least a second conductive electrode comprising a second fuel cell catalyst; and

a proton exchange membrane separating the first conductive electrode and the second conductive electrode;

5 wherein the first fuel cell catalyst and the second fuel cell catalyst are independently selected catalysts according to any of claims 24 through 49.

51. The electrode membrane combination according to claim 50, wherein said first fuel cell catalyst and said second fuel cell catalyst are the same materials.

52. The electrode membrane combination according to claim 50, wherein
10 said proton exchange membrane has a thickness ranging from about 2 μm to about 100 μm .

53. The electrode membrane combination according to claim 50, wherein said proton exchange membrane comprises a material selected from the group consisting of Nafion, silicon oxide Nafion composite, polyphosphazenes, sulfonated (PPO), and , silica-polymer composites.

54. The electrode membrane combination according to claim 50, wherein
15 the first conductive electrode and the first fuel cell catalyst form separate layers.

55. The electrode membrane combination according to claim 54, wherein the first conductive layer and first fuel cell catalyst further include a microdiffusion layer between the electrode and the catalyst.

56. The electrode membrane combination according to claim 50, wherein
20 the first conductive electrode and the first fuel cell catalyst form an integral single layer.

57. The electrode membrane combination according to claim 56, wherein said first fuel cell catalyst additionally acts as a microdiffusion layer.

58. The electrode membrane combination according to claim 56, wherein
25 the second conductive electrode and the second fuel cell catalyst form an integral single layer.

59. The electrode membrane combination according to claim 58, wherein said second fuel cell catalyst additionally acts as a microdiffusion layer.

60. A fuel cell stack comprising a plurality of electrically connected electrode membrane combinations said electrode membrane combinations comprising:

5 at least a first conductive electrode comprising a first fuel cell catalyst;

at least a second conductive electrode comprising a second fuel cell catalyst; and

10 a proton exchange membrane separating the first conductive electrode and the second conductive electrode;

wherein the first fuel cell catalyst and the second fuel cell catalyst are independently selected catalysts according to any of claims 24 through 48.

61. An electrical device comprising the fuel cell stack according to claim 60.

15 62. The device of claim 61, wherein said device is a transportation vehicle.

63. A battery replacement wherein said battery replacement comprises a container containing a fuel cell stack according to claim 60, and wherein said container provides a positive electrode terminal and a negative electrode terminal for contacting to a
20 device requiring electricity.

64. The battery replacement according to claim 63, wherein said battery replacement powers a home, a cell phone, a lighting system, a computer, and/or an appliance.

25 65. A method of fabricating a fuel catalyst, said method comprising:
providing a plurality of nanoparticles; and
depositing on said nanoparticles a substantially continuous thin film comprising platinum or a platinum alloy.

66. The method of claim 65, wherein said depositing is by a method selected from the group consisting of sputtering deposition, chemical vapor deposition (CVD), molecular beam epitaxy (MBE), plasma-assisted vapor deposition, and electron beam evaporation deposition.

5 67. The method of claim 65, wherein said thin film partially covers the nanoparticles.

68. The method of claim 65, wherein the nanoparticles are fully coated with said thin film.

69. The method of claim 65, wherein said thin film ranges in thickness
10 from about 1 to about 500 angstroms.

70. The method of claim 69, wherein said thin film ranges in thickness from about 5 to about 100 angstroms.

71. The method of claim 65, wherein said thin film comprises an alloy comprising platinum (Pt), vanadium (V), and one or more metals selected from the group
15 consisting of Co, Ni, Mo, Ta, W, and Zr.

72. The method of claim 71, wherein said thin film comprises an alloy comprising platinum (Pt), vanadium (V), and one or more metals selected from the group consisting of Co, and Ni.

73. The method of claim 71, wherein platinum comprises up to about
20 12% of said alloy.

74. The method of claim 73, wherein said alloy contains platinum, vanadium, nickel, and copper.

75. The method of claim 71, wherein said thin film comprises an alloy having the formula:

25
$$\text{Pt}_x\text{V}_y\text{Co}_z\text{Ni}_w$$

wherein:

x is greater than 0.06 and less than 1;

y, z, and w are independently greater than zero and less than 1;

$x + y + z + w = 1$.

76. The method of claim 75, wherein x is 0.12.

5 77. The method of claim 75, wherein x is 0.12, y is 0.07, z is 0.56, and w is 0.25.

78. The method of claim 65, wherein said nanoparticles are attached to a substrate.

10 79. The method of claim 78, wherein said nanoparticles are attached to a porous carbon substrate.

80. The method of claim 78, wherein said nanoparticles are attached to a porous electrode.

81. The method of claim 78, wherein said nanoparticles are electrically coupled to a porous electrode.

15 82. The method of claim 78, wherein said nanoparticles are attached to a polymer electrolyte membrane substrate.

83. The method of claim 65, wherein said nanoparticles are selected from the group consisting of nanotubes, nanofibers, nanohorns, nanopowders, nanospheres, and quantum dots.

20 84. The method of claim 65, wherein said nanoparticles are carbon nanotubes.

85. The method of claim 84, wherein said nanoparticles are nanotubes having a length less than about length less than 50 μm and a width less than about 100 nm.

25 86. The fuel cell catalyst of claim 85, wherein said nanoparticles are nanotubes having a diameter of about 50 nm to about 100 nm.

87. A method of preparing a fuel cell element, said method comprising:
providing a plurality of fibers and/or a porous electrode material;
depositing a nanoparticle catalyst on said plurality of fibers and/or
porous electrode material;

5 forming nanoparticles on said plurality of fibers and/or porous
electrode material using said nanoparticles catalyst;

forming a catalytically active layer comprising a substantially
continuous thin film on said nanoparticles thereby forming a fuel cell element comprising a
plurality of fibers bearing nanoparticles partially or fully coated with a catalytically active
10 thin film.

88. The method of claim 87, wherein said plurality of fibers comprises a
plurality of carbon fibers.

89. The method of claim 88, wherein said plurality of carbon fibers
comprise a porous electrode.

15 90. The method of claim 88 wherein said plurality of fibers comprise a
carbon fiber paper.

91. The method of claim 87, wherein said nanoparticle catalyst is a
carbon nanotube catalyst and said nanoparticles are carbon nanotubes.

20 92. The method of claim 91, wherein said nanoparticles are formed by
chemical vapor deposition (CVD).

93. The method of claim 87, wherein said depositing a nanoparticle
catalyst comprises depositing said catalyst on said fibers by chemical vapor deposition
(CVD).

25 94. The method of claim 91, wherein said catalyst is a catalyst selected
from the group consisting of $\text{Co}_{1-x}\text{Mo}_x$ where $0 \leq x \leq 0.3$, $\text{Co}_{1-x-y}\text{Ni}_x\text{Mo}_y$ where $0.1 \leq x \leq 0.7$ and
 $0 \leq y \leq 0.3$, $\text{Co}_{1-x-y-z}\text{Ni}_x\text{V}_y\text{Cr}_z$ where $0 \leq x \leq 0.7$ and $0 \leq y \leq 0.2$, $0 \leq z \leq 0.2$, $\text{Ni}_{1-x-y}\text{Mo}_x\text{Al}_y$ where
 $0 \leq x \leq 0.2$ and $0 \leq y \leq 0.2$, and $\text{Co}_{1-x-y}\text{Ni}_x\text{Al}_y$ where $0 \leq x \leq 0.7$ and $0 \leq y \leq 0.2$.

95. The method of claim 91, wherein said catalyst is a catalyst selected from the group consisting of $\text{Co}_{8.8}\text{Mo}_{1.2}$, $\text{Co}_{2.2}\text{Ni}_{5.6}\text{Mo}_{2.2}$, $\text{Co}_{5.7}\text{Ni}_{2.1}\text{V}_{1.1}\text{Cr}_{1.1}$, $\text{Ni}_{8.0}\text{Mo}_{1.0}\text{Al}_{1.0}$, and $\text{Co}_{6.4}\text{Ni}_{2.4}\text{Al}_{1.2}$.

5 96. The method of claim 91, wherein said nanotubes have a length less than $50\text{ }\mu\text{m}$ and a width less than about 100 nm .

97. The method of claim 91, wherein said nanotubes have a diameter of about 50 nm to about 100 nm .

98. The method of claim 91, wherein said nanoparticles are coated with a substantially continuous thin film comprising platinum or a platinum alloy.

10 99. The method of claim 98, wherein said thin film partially covers the nanoparticles.

100. The method of claim 98, wherein the nanoparticles are fully coated with said thin film.

15 101. The method of claim 98, wherein said thin film ranges in thickness from about 1 to about 1000 angstroms.

102. The method of claim 100, wherein said thin film ranges in thickness from about 5 to about 500 angstroms.

103. The method of claim 100, wherein said thin film ranges in thickness from about 5 to about 100 angstroms.

20 104. The method of claim 103, wherein said thin film comprises an alloy comprising platinum (Pt), vanadium (V), and one or more metals selected from the group consisting of Co, Ni, Mo, Ta, W, and Zr.

25 105. The method of claim 104, wherein said thin film comprises an alloy comprising platinum (Pt), vanadium (V), and one or more metals selected from the group consisting of Co, and Ni.

106. The method of claim 104, wherein platinum comprises up to about 50% (mole ratio or atomic percentage) of said alloy.

107. The method of claim 104, wherein platinum comprises up to about 12% (mole ratio or atomic percentage) of said alloy.

5 108. The method of claim 104, wherein said alloy contains platinum, vanadium, nickel, and copper.

109. The method of claim 104, wherein said thin film comprises an alloy having the formula:



10 wherein:

x is greater than 0.06 and less than 1;

y, z, and w are independently greater than zero and less than 1;

$x + y + z + w = 1$.

110. The method of claim 109, wherein x is 0.12.

15 111. The method of claim 109, wherein x is 0.12, y is 0.07, z is 0.56, and w is 0.25.

112. The method of claim 87, wherein:

said providing a plurality of fibers and/or a porous electrode material comprises providing a carbon fiber paper;

20 said depositing a nanoparticle catalyst comprises depositing said catalyst by chemical vapor deposition;

said forming nanoparticles comprises forming carbon nanotubes; and

said forming a catalytically active layer comprising depositing a substantially continuous thin film comprising platinum or a platinum alloy.

25 113. A method of making a carbon nanotube for use in a fuel cell, said method comprising:

providing a nanotube growth catalyst selected from the group consisting of $\text{Co}_{1-x}\text{Mo}_x$ where $0 \leq x \leq 0.3$, $\text{Co}_{1-x-y}\text{Ni}_x\text{Mo}_y$ where $0.1 \leq x \leq 0.7$ and $0 \leq y \leq 0.3$, Co_{1-x} .

$_{y-z}\text{Ni}_x\text{V}_y\text{Cr}_z$ where $0 \leq x \leq 0.7$ and $0 \leq y \leq 0.2$, $0 \leq z \leq 0.2$, $\text{Ni}_{1-x-y}\text{Mo}_x\text{Al}_y$ where $0 \leq x \leq 0.2$ and $0 \leq y \leq 0.2$, and $\text{Co}_{1-x-y}\text{Ni}_x\text{Al}_y$ where $0 \leq x \leq 0.7$ and $0 \leq y \leq 0.2$; and

forming a carbon nanotube on said catalyst.

114. The method of claim 113, wherein said catalyst is a catalyst selected
5 from the group consisting of $\text{Co}_{8.8}\text{Mo}_{1.2}$, $\text{Co}_{2.2}\text{Ni}_{5.6}\text{Mo}_{2.2}$, $\text{Co}_{5.7}\text{Ni}_{2.1}\text{V}_{1.1}\text{Cr}_{1.1}$, $\text{Ni}_{8.0}\text{Mo}_{1.0}\text{Al}_{1.0}$, and $\text{Co}_{6.4}\text{Ni}_{2.4}\text{Al}_{1.2}$.

115. The method of claim 113, wherein said forming is by chemical vapor deposition (CVD).

116. A carbon nanotube, said nanotube comprising a nanotube growth
10 catalyst selected from the group consisting of $\text{Co}_{1-x}\text{Mo}_x$ where $0 \leq x \leq 0.3$, $\text{Co}_{1-x-y}\text{Ni}_x\text{Mo}_y$ where $0.1 \leq x \leq 0.7$ and $0 \leq y \leq 0.3$, $\text{Co}_{1-x-y-z}\text{Ni}_x\text{V}_y\text{Cr}_z$ where $0 \leq x \leq 0.7$ and $0 \leq y \leq 0.2$, $0 \leq z \leq 0.2$, $\text{Ni}_{1-x-y}\text{Mo}_x\text{Al}_y$ where $0 \leq x \leq 0.2$ and $0 \leq y \leq 0.2$, and $\text{Co}_{1-x-y}\text{Ni}_x\text{Al}_y$ where $0 \leq x \leq 0.7$ and $0 \leq y \leq 0.2$.

117. The carbon nanotube of claim 116, wherein said catalyst is a catalyst
15 selected from the group consisting of $\text{Co}_{8.8}\text{Mo}_{1.2}$, $\text{Co}_{2.2}\text{Ni}_{5.6}\text{Mo}_{2.2}$, $\text{Co}_{5.7}\text{Ni}_{2.1}\text{V}_{1.1}\text{Cr}_{1.1}$, $\text{Ni}_{8.0}\text{Mo}_{1.0}\text{Al}_{1.0}$, and $\text{Co}_{6.4}\text{Ni}_{2.4}\text{Al}_{1.2}$.

118. A catalyst for growing a carbon nanotube for use in a fuel cell, said
catalyst being catalyst selected from the group consisting of $\text{Co}_{1-x}\text{Mo}_x$ where $0 \leq x \leq 0.3$, $\text{Co}_{1-x-y}\text{Ni}_x\text{Mo}_y$ where $0.1 \leq x \leq 0.7$ and $0 \leq y \leq 0.3$, $\text{Co}_{1-x-y-z}\text{Ni}_x\text{V}_y\text{Cr}_z$ where $0 \leq x \leq 0.7$ and $0 \leq y \leq 0.2$, $0 \leq z \leq 0.2$, $\text{Ni}_{1-x-y}\text{Mo}_x\text{Al}_y$ where $0 \leq x \leq 0.2$ and $0 \leq y \leq 0.2$, and $\text{Co}_{1-x-y}\text{Ni}_x\text{Al}_y$ where $0 \leq x \leq 0.7$ and
20 $0 \leq y \leq 0.2$.

119. The catalyst of claim 118, wherein said catalyst is selected from the
group consisting of $\text{Co}_{8.8}\text{Mo}_{1.2}$, $\text{Co}_{2.2}\text{Ni}_{5.6}\text{Mo}_{2.2}$, $\text{Co}_{5.7}\text{Ni}_{2.1}\text{V}_{1.1}\text{Cr}_{1.1}$, $\text{Ni}_{8.0}\text{Mo}_{1.0}\text{Al}_{1.0}$, and $\text{Co}_{6.4}\text{Ni}_{2.4}\text{Al}_{1.2}$.